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Determination of Aldicarb Residues in Water by Combined High Performance Liquid Chromatography/Mass Spectrometry

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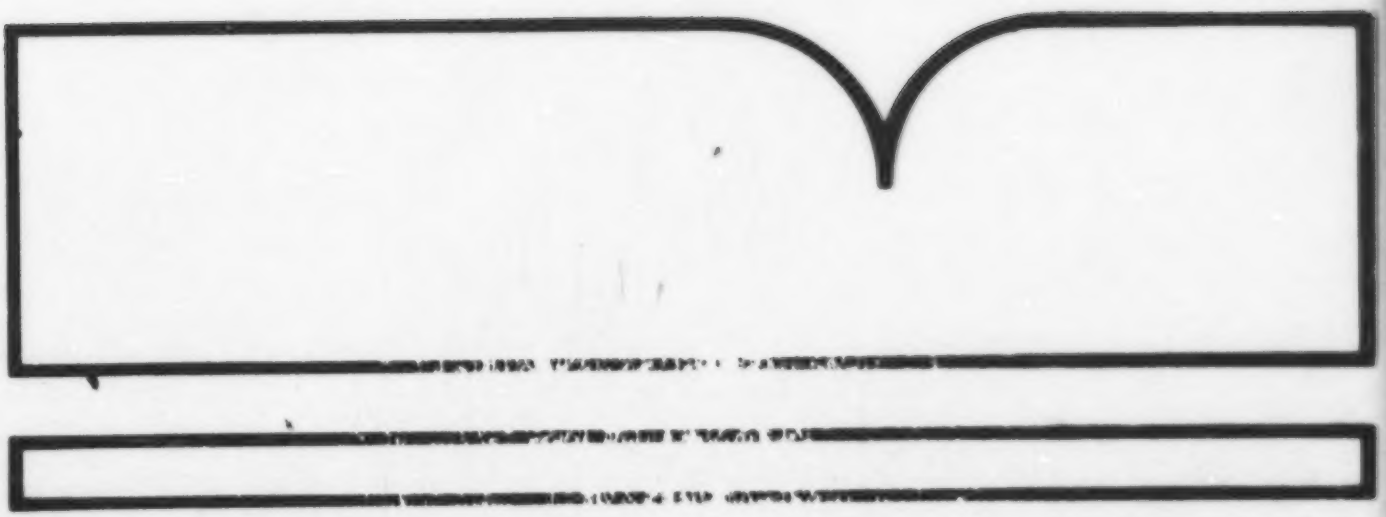

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16. ABSTRACT

Current gas chromtographic methods for the analysis of aldicarb (Temik) residues involve a number of time consuming steps including a liquid chromatographic separation of the residues, conversions to derivatives or common intermediates, and separate analyses of the intermediates. Recently, methods based on reverse phase high performance liquid chromatograph (LC) have reduced analytical times, but due to the lack of a highly specific detector, extensive clean-up steps may still be required.

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Determination of Aldicarb Residues in Water by Combined High Performance Liquid Chromatography/Mass Spectrometry

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Current gas chromatographic methods for the analysis of aldicarb (Temik) residues involve a number of time consuming steps including a liquid chromatographic separation of the residues, conversions to derivatives or common intermediates, and separate analyses of the intermediates (MAITLEN et al. 1968, GALOUX et al. 1979). Recently, methods based on reverse phase high performance liquid chromatography (LC) have reduced analytical times, but, due to the lack of a highly specific detector, extensive clean-up steps may still be required (KRAUSE 1980, COCHRANE & LANOUETTE 1981).

The recent contamination of well waters in certain agricultural areas prompted us to develop a method based on combined liquid chromatography/mass spectrometry (LC/MS). The new method has advantages of speed and sensitivity when applied to the determination of aldicarb, aldicarb sulfoxide, and aldicarb sulfone. A modification of the chromatographic conditions has shown promise for the inclusion of aldicarb oxime and aldicarb oxime sulfoxide into the scheme without increasing the analysis time. Aldicarb oxime sulfone has not been investigated but should readily fit into the modified procedure.

EXPERIMENTAL

Standards and reagents. Solvents were "Distilled-in-Glass", UV grade (Burdick and Jackson Laboratories, Inc., Muskegon, MI). Glass wool and anhydrous sodium sulfate were pre-extracted with hexane and dried. Analytical standards of aldicarb, aldicarb sulfoxide, aldicarb sulfone, aldicarb oxime, and aldicarb oxime sulfoxide were obtained from the EPA Reference Standards Repository, RTP, NC.

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Instrumentation. Liquid chromatography was performed with Tracor Model 995 pump equipped with a Rheodyne 7125 loop injector, a Tracor 970 variable wavelength detector at 210 nm, and a duPont 15 cm X 4.2 mm i.d. nitrile column. For quantitative trials 50 uL aliquots were injected into a 100 uL loop. The chromatograph was operated isocratically with 2-propanol/hexane (3:7) at a flow of 1.2 mL/min.

A Finnigan 3200 chemical ionization mass spectrometer equipped with the manufacturer's 6000 series data system and liquid chromatograph interface was used. The reagent gas was methane. Spectrometer operating conditions were: 110 eV electron energy, 1.0 mA emission current, 1800 V multiplier voltage, 10exp-8 amps/volt preamp setting, source temperature 120 C. The LC/MS interface vaporizer and cleanup heater readings were 120 C and 150 C, respectively. The drive chamber was maintained under a nitrogen blanket with the infrared heater at full power. Data for quantification was collected by select ion monitoring (SIM) at the masses listed in Table 1.

Extraction. A 200 mL sample of water was transferred to a 500 mL separatory funnel and extracted with two 20 mL portions of dichloromethane. For each extraction the funnel was shaken one min, the layers allowed to separate, and the organic layer dried by passage through a glass column (2.5 cm i.d. x 10 cm, with the tip drawn down to a 6 mm opening) packed with a small plug of glass wool followed by a 5 cm layer of anhydrous sodium sulfate. After the extracts were dried, the sodium sulfate column was rinsed with two 2 mL portions of hexane and the rinses combined with the extracts. The solvent volume was reduced to about 0.5 mL under a gentle stream of dry nitrogen and then brought back to approximately 5 mL by the addition of hexane. The extracts were refrigerated until immediately before the LC/MS analyses; then they were reduced under a nitrogen stream to 1.0 mL volume.

RESULTS AND DISCUSSION

The extraction procedure was tested by fortification at a 5 ppb level. Average recoveries of 57% for aldicarb, 110% for aldicarb sulfone, and 101% for aldicarb sulfoxide were obtained from 3 replicate determinations with standard deviations of less than 7%. Modifications to the extraction procedure should bring the aldicarb recovery in line with the higher values reported by others (eg. GALOUX et al. 1979).

The salient features of the methane chemical ionization mass spectra of aldicarb and its metabolites are presented in Table 1. The selected ion monitoring (SIM) masses are those used in the well water analyses. In some cases the more intense ions in the 85-88 m/z region would have been preferable for lower limits of detection, but this region of the mass spectrum is subject to interference from traces of hexane which manage to pass through the LC/MS interface.

TABLE 1

Significant Ions in the Methane Chemical Ionization Mass Spectra of Aldicarb Residues.

Compound	SIM Quantification	SIM Confirmation	Other Significant Ions
	m/z (relative abundance)		
Aldicarb	89 (100)	116 (12)	85 (11), 86 (5)
Aldicarb sulfoxide	132 (31)		86 (100)
Aldicarb sulfone	148 (67)	223 (0.6)	166 (3)
Aldicarb oxime			86 (100), 87 (11) 89 (36)
Aldicarb oxime sulfoxide			86 (100)

The linearity of system response has not been tested; however, extensive tests on a number of other carbamate pesticides predict a linear response from the sub-nanogram region to greater than 100 ng (WRIGHT 1982).

The detection of various concentrations of diferent aldicarb residues by SIM is illustrated in Figures 1-3. The absence of the confirming ion at low ppb levels of aldicarb and aldicarb sulfone is to be expected on the from the low relative abundance of these ions. The limits of detection obtained by the LC/MS method are presented in Table 2 in conjunction with values reported for other methods. There is no consistent definition of limit of detection among these methods; we report values which produced a response of greater than 2:1 signal-to-noise.

TABLE 2

Limits of Detection for Aldicarb Residues ppb(ng)

Method	LC/MS	LC/UV	LC/Fluoro-metric	GC/Hall
Reference	this work	SPARACINO & HINES (1976)	KRAUSE (1979)	GALOUX et al (1979)
Compound				
Aldicarb	0.3 (3)	(5.3)	(<1)	0.05
Aldicarb sulfoxide	0.6 (6)	(27.0)	(<1)	
Aldicarb sulfone	0.3 (3)	(61.3)	(<1)	

The MS compares favorably with the other detectors in terms of sensitivity, and the selectivity of the MS is an added advantage. In the sample whose UV detected chromatogram is illustrated in Figure 4 aldicarb and its sulfone are readily determined by both detectors, but the sulfoxide is masked in the UV by co-eluants whereas the ion current profile shows no such interference. In more complex sample matricies this advantage of MS detection may become even more important.

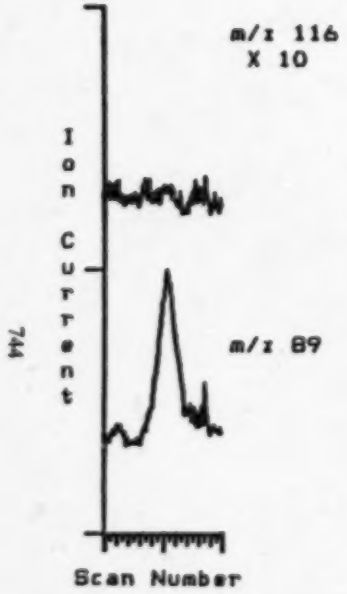

FIGURE 1. HPLC/MS SIM detection of 2 ppb aldicarb.

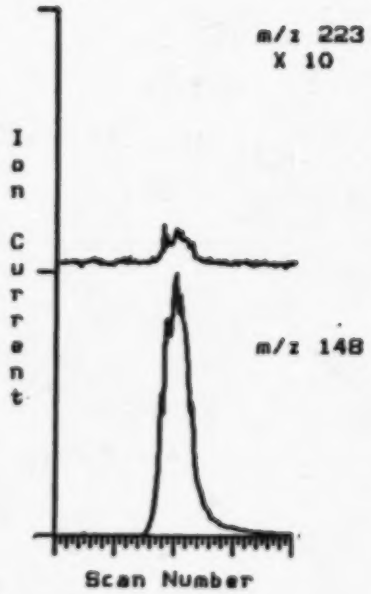

FIGURE 2. HPLC/MS SIM detection of 53 ppb aldicarb sulfone.

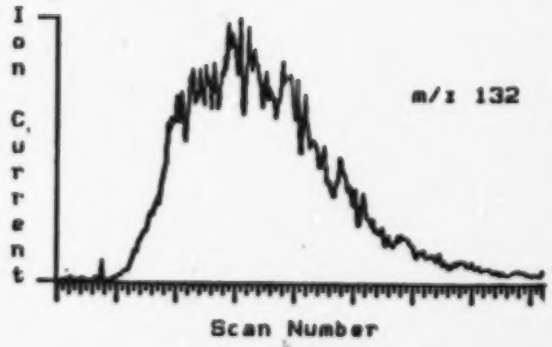

FIGURE 3. HPLC/MS SIM detection of 64 ppb aldicarb sulfoxide.

The chromatography conditions described in the experimental section were devised for a high priority analysis and are essentially an extraction of isocratic conditions for optimum turn- around time from a general carbamate gradient elution scheme (SPARACINO & HINES 1976, WRIGHT 1982). It later became obvious that significant improvements in the method might be possible. The limits of detection might be improved by accessing the more intense ions in the m/z 85-88 region or by changing the LC conditions to increase the quantity of material delivered to the spectrometer per unit time. The 1.2 mL/min flow originally used was mandated by the capacity of the LC/MS interface for the 2-propanol/hexane (3:7) mixture. By changing from hexane to pentane the low mass solvent interference could be reduced and the solvent volatility increased. By replacing the 2-propanol with a methanol/2-propanol (1:9) mixture an increase in polarity was obtained which permitted a significant reduction in the amount of alcohol required for elution of the residues and further increased the solvent volatility. The solvent composition finally settled on was a methanol/ 2-propanol/pentane (1:9:40) mixture. With this combination a flow of 2.0 mL/min was accomodated by the LC/MS interface. Methanol/2-propanol combinations were also tried, but proved unsatisfactory. The two chromatography systems are illustrated in Figures 5 and 6.

At this point the oximes were also included in the LC/MS portion of the analysis. These compounds are included in the illustrative chromatogram, Figure 6. Several points should be noted here. First, with the three component solvent system, all five of the aldicarb residues can be included in one 15 minute LC/MS analysis. Second, the aldicarb sulfoxide peak, which was broad and tailed badly with the 2-propanol/hexane system, now is significantly sharper and shows little evidence of tailing. Both of these features should contribute to a lowering of the limit of detection. And finally, the elution order of aldicarb sulfoxide and aldicarb sulfone has been reversed.

In summary, the LC/MS analysis of aldicarb residues compares favorably with other methods in terms of sensitivity. It has major advantages in terms of the time required for the analysis of multiple aldicarb residues since only a minimum clean-up is required, no derivatization steps are necessary, and at least five different residues can be quantified in one experiment.

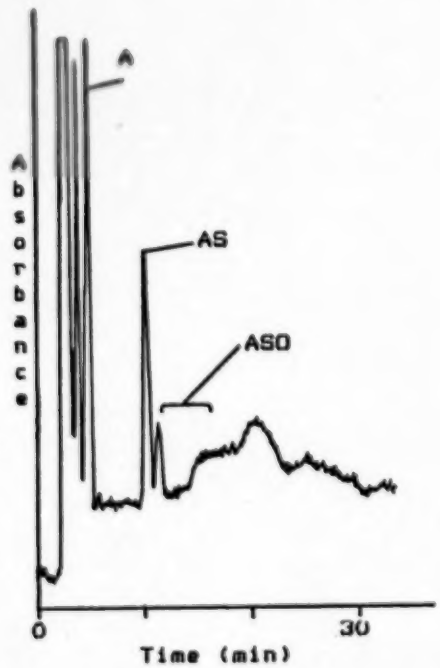

FIGURE 4. HPLC/UV of well water extract. 210 nm. 3:7 2-propanol/hexane. 1.2 mL/min.

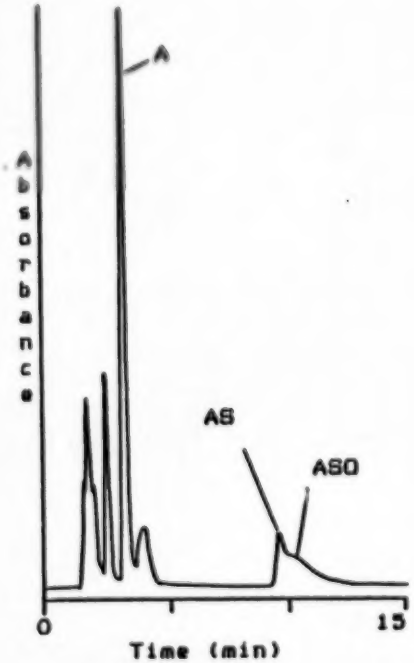

FIGURE 5. HPLC/UV of three aldicarb standards. 210 nm. 3:7 2-propanol/hexane. 1.2 mL/min.

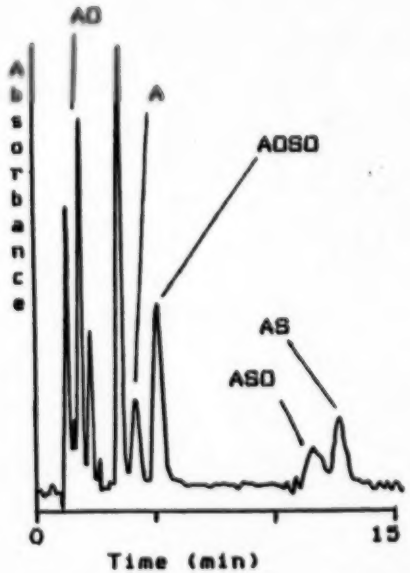

FIGURE 6. HPLC/UV of five aldicarb standards. 210 nm. 1:9:40 methanol/2-propanol/ hexane. 2.0 mL/min.

Legend: A=aldicarb, AS=aldicarb sulfone, ASO=aldicarb sulfoxide, AO=aldicarb oxime, AOSO=aldicarb oxime sulfoxide

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